California Environmental Protection Agency

Air Resources Board

Northern Laboratory Branch
Monitoring and Laboratory Division

SOP MLD 022

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF CARBONYL COMPOUNDS IN AMBIENT AIR

EFFECTIVE DATE: January 1, 2001
APPROVAL DATE: October 5, 1998
REVISION NUMBER: 4.1

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedure are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

State of California
Air Resources Board
Monitoring & Laboratory Division

S.O.P. MLD 022

Standard Operating Procedure for the Determination of Carbonyl Compounds in Ambient Air

1 Scope

This procedure describes the analysis of formaldehyde, acetaldehyde, and methyl ethyl ketone (MEK) in the ambient air by High Performance Liquid Chromatography (HPLC) utilizing a solid adsorbent. This method is based on the U.S. EPA Method TO-11. In this revision of the SOP, an ozone scrubber is installed upstream from the sampling cartridge. In addition, the silica sampling cartridge is found to be more efficient in collecting formaldehyde from the ambient air than the C-18 cartridge which was used in the previous Revision, 3.0 . Silica cartridges, also have a lower level of acetone contamination than C-18 cartridges.

2 Summary of Method

2.1 Ambient air is drawn through chromatographic grade Sep-Pak silica cartridges. The cartridges are coated with acidified 2,4-dinitrophenylhydrazine (DNPH). The sampling rate is 0.7L per minute for a 24-hour period. During sampling, formaldehyde, acetaldehyde, and methyl ethyl ketone react with the DNPH to form derivatives that are called hydrazones.

2.2 The DNPH derivatives are eluted from the sampling cartridges using acetone-free acetonitrile (ACN) and are quantified using reverse-phase HPLC with ultraviolet absorption detection at 360 nm.

3 Interferences/Limitations

3.1 Since this procedure is written for the sampling and analysis of formaldehyde, acetaldehyde, and methyl ethyl ketone, possible interferences may be caused by the coelution of other aldehydes and ketones.

3.2.1 When commercially pre-coated DNPH cartridges are used, 5% of each production lot must be analyzed for impurities prior to use.

4 Apparatus

4.1 A Waters gradient HPLC system consisting of mobile phase reservoirs; high pressure pumps; an injection valve or automatic sampler; a Waters Nova-Pak C-18 column (3.9 mm x 15 cm); a variable wavelength UV detector operating at 360 nm; and a data system.

4.2 Sampling system - a XonTech Module 920 Multi-media sampler fitted with a sampling head configured to hold the Sep-Pak DNPH-silica cartridges and capable of sampling at a flow rate of between 0.5 and 2.0 LPM.

4.3 Supelco 4 mL glass vials with Teflon lined screw caps. Sun brokers 1 mL autosampler "Sun Vial" with polyethylene cap septum.

4.4 Sample rack to hold cartridges during elution.

4.5 Filtration and degassing system for mobile phase solvents such as Waters Part #85124.

4.6 Various volumetric pipets and flasks and graduated cylinders.

4.7 Polyethylene gloves - used to handle the treated cartridges.

4.8 Whatman 3.7 cm, #41 ashless filter paper.

5 Reagents

5.2 Acetone-Free Acetonitrile and water mobile phase solvents, HPLC grade such as Burdick & Jackson Product #016 and Baker #4218-3, respectively.

5.3 Sep-Pak DNPH-silica cartridges - Waters Chromatography.

5.4 Calibration Standards solutions or hydrazone crystals can be purchased from Radian Corporation or Supelco.

5.5 Potassium iodide --A.C.S. reagent grade.

6 Preparation of DNPH-Carbonyl Standards and Ozone Scrubber

6.1 Standard Preparation

6.1.1 Prepare a standard stock solution of the DNPH-carbonyl derivative by dissolving 10mg of hydrazone crystals in 100 mL of acetonitrile (acetone-free). Custom stock solutions are also available from Radian.

6.1.2 Prepare a working calibration standard mix from the laboratory or vendor standard

stock solution using acetonitrile (acetone-free). The concentration of the DNPH-carbonyl compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample. The working standard concentrations should be 0.05, 0.50, and 2.00ug/mL as aldehyde or ketone. In order to facilitate the calculation process, the latter concentrations are replaced with 0.25, 2.5 and 10ug/5ml, respectively since the hydrazones are collected in 5mL volumetric flask.

6.1.3 Store all standard solutions in a refrigerator. They are stable for 4 months.

6.2 Ozone Scrubber Preparation

6.2.1 Prepare a 0.6M KI in deionizied water. Dip the 3.7cm Whatman filter into the KI solution twice and let it dry. Upon drying, the filter should be placed between the two black rings and assembled.

7 Sampling

7.1 A XonTech Model 920 sampler is used to draw the ambient sample through the cartridges.

7.2 Remove the Sep-Pak cartridge and ozone scrubber from the transport containers. Place the cartridge and ozone scrubber in the appropriate holders and make sure that the holders are tightened properly.

7.3 Expose the Sep-Pak cartridge to 0.7 LPM ambient air for 24 hours. After the run, remove the Sep-Pak cartridge, recap it and put it back in the transport container along with the 920 "printout" for the sampling period.

7.4 The aldehyde sampling is to be done on the same schedule as that for "Toxics" and therefore the transport container can be placed in the canister box for shipment back to the lab.

7.5 Upon receipt at the lab, the Sep-Pak should be placed in cold storage until elution.

8 Sample Analysis

8.1 Sample Desorption

8.1.1 Remove the Sep-Pak cartridges from the transport tube and connect each to a clean syringe.

8.1.2 Place the cartridge/syringe in the syringe rack and backflush the cartridge (gravity feed) with 5 mL of acetonitrile (acetone-free) to a 5 mL volumetric flask. If the sample is not transferring into the flask then use a plunger to transfer the sample drop by drop.

8.1.3 Dilute to the 5 mL mark with ACN (acetone-free). Label the flask with sample ID.

8.2 HPLC Operating Parameters

8.2.1 The operating parameters are shown in Appendix I.

8.2.2 Equilibrate the column for 30 minutes before first analysis. Analyze a blank to check for method interferences.

8.2.3 Calibrate the instrument using three different standards (0.25, 2.50, and 10.0ug/5ml). Linearity is indicated by an r of at least 0.999.

8.2.4 Check the calibration of the instrument for each run by analyzing a control sample (5ug/5mL). The concentration given must fall within the UCL and LCL of the control sample value ($\pm$ 3 assigned RSD).

8.2.5 Run one injection per sample and a control standard for every ten samples.

9.0 Quality Control

9.1 Solvent and Cartridge Blank

A solvent blank must be analyzed before any standard or sample is run. The solvent blank must not contain formaldehyde, acetaldehyde, or MEK at concentration level greater than the LOD in order to validate any subsequently analyzed samples. The blank DNPH-silica cartridges are analyzed for contamination. 5% of each production lot must be analyzed for impurities prior to use. The blank cartridges must not contain any analytes with concentrations greater than 2X LOD. If the concentrations are greater than 2X LOD, then the cartridges shall be discarded.

9.2 Multipoint Analysis Verification

A multipoint analysis must be performed at least once per calendar year to verify the precision and the calibration working range. This is done by analyzing at least five standards of different concentrations with 4 injections at each concentration level.

A multipoint calibration is also required under the following conditions:

a.) When the column is changed.

b.) When major maintenance is performed.

c.) When there is a change in the matrix or a reagent.

9.3 Limit of Detection (LOD) Verification

The LOD must also be verified on a yearly basis, or when the same conditions as listed under the multipoint calibration verification occur. This is done by analyzing a minimum of seven replicates of a solution containing the analytes at a concentration of 0.10ug/5mL (0.02ug/mL).

The LOD is estimated using the following equation, as specified in Section 9.1 of the ELB Quality Control Manual

$$LOD = t_{(n-1,\ 1-\alpha = 99\%)} \times S$$

$t_{(n-1,\ 1-\alpha = 99\%)}$ = student's T-distribution value at n-1 degrees of freedom

S = standard deviation

Formaldehyde	0.10 ug/5ml
Acetaldehyde	0.10 ug/5ml
MEK	0.10 ug/5ml

All subsequent LOD verifications must be equal to or less than these values. The published LOD for target analytes analyzed by this method and example verification values are presented in Appendix II, page 10.

9.4 Daily Calibration

A three-point calibration curve is calculated for each analytical run using calibration standards with concentrations 0.25, 2.50, and 10.0ug/5mL as aldehyde or keytone. Linearity is indicated if the correlation coefficient is 0.999.

9.5 Control Standard

Analytical results of this standard are recorded and used to generate control charts. The upper and lower control limits are set at ± three times the assigned standard deviation (SD) from the average. The upper and lower warning limits are set at ± two times the assigned SD from the average. This provides minimum upper and lower control limits of ± 15 % and upper and lower warning limits of ± 10 %. Control standard results must be within the established control limits for the analytical run to be valid. If the control limits are violated, then the problem should be resolved. The samples in between the "good" control and "bad" control can be re-analyzed once control has been achieved.

9.6 Method Precision

Sample precision is measured by the analysis of ambient duplicate samples. The frequency of duplicate analyses is 10% of the total ambient samples analyzed. Maximum allowable percent differences (PD) for the duplicate sample analyses are $\pm$ 15% for formaldehyde and acetaldehyde which is the same as the control limits for the control standard. For MEK, the maximum allowable percent difference is 37.8%. This PD was determined by making 20 injections of an ambient sample with a concentration near the MEK LOD (0.10ug/5mL). This method was used since ambient concentrations of MEK are typically near the LOD and require a larger PD. If the measured PD is greater than the maximum allowable PD, then the samples in between the "good duplicate pair and "bad" duplicate pair must be re-analyzed once the problem has been resolved.

9.7 Method Accuracy

Method accuracy is determined by measuring the recovery of a spiked sample. A spiked sample is prepared by placing 950ul of an extracted sample into an autosampler vial and adding 50ul of the spiking standard. The concentration of the spiking standard is 10ug/mL. The percent recovery is calculated as follows:

$$\text{Percent Recovery} = \frac{(M1 - M2) * 100}{C}$$

M1 = Measured conc. of spiked sample
M2 = Measured sample conc.
C = Actual conc. of spike (2.5ug/5mL)

For a valid spike analysis, the percent recovery should be between 70 to 130%. If the percent recovery is outside this range, then a problem is present which needs to be corrected. After correcting the problem, re-analyze the sample and spiked sample.

10.0 **Calculations**

10.1 Concentrations are reported as ppbv and are calculated as follows:

$$ppbv = \frac{(24.478 * 10^9) * G}{MW * V}$$

G = grams of carbonyl
V = volume of air collected in liters
MW = molecular weight of carbonyl (grams / mole)

Formaldehyde = 30.0162 g/mole
Acetaldehyde = 44.0530 g/mole
MEK = 72.1066 g/mole

APPENDIX I

OPERATING PARAMETERS FOR LIQUID CHROMATOGRAPHY

Column: Nova-Pak C-18 (3.9mm x 150mm) operated @ room temperature.

Gradient Program:	Time (min)	%A	%B	%C
	0.0	100	0	0
	2.0	100	0	0
	13.0	25	75	0
	13.5	0	0	100
	14.5	0	0	100
	15.0	100	0	0
	21.0	100	0	0

where:

A = 60% Water: 30% Acetonitrile: 10% THF
B = 60% Acetonitrile: 40% Water
C = 100% Acetonitrile

Detector: Waters Model 486 UV/VIS at 360 nm. Sample rate 2 point/sec and 1.00 AUFS.

Flow Rate/Run Time/Injection Volume: 1.0 mL/min.; 22 minute run; 20 uL.

Retention Time:

Formaldehyde	~	5.0 minutes
Acetaldehyde	~	7.3 minutes
MEK	~	16.0 minutes

APPENDIX II

TARGET ANALYTE LODS AND HIGHEST CALIBRATION CONCENTRATION

RADIAN 324617-69, 03/28/02

Target Compound	Published LOD (ug/5ml)	Calculated LOD (ug/5ml)	Correlation Coefficient R	Highest Calibrated Conc. (ug/5ml)
Formaldehyde	0.10	0.01	0.99996	10.0
Acetaldehyde	0.10	0.01	0.99996	10.0
MEK	0.10	0.02	0.99989	10.0